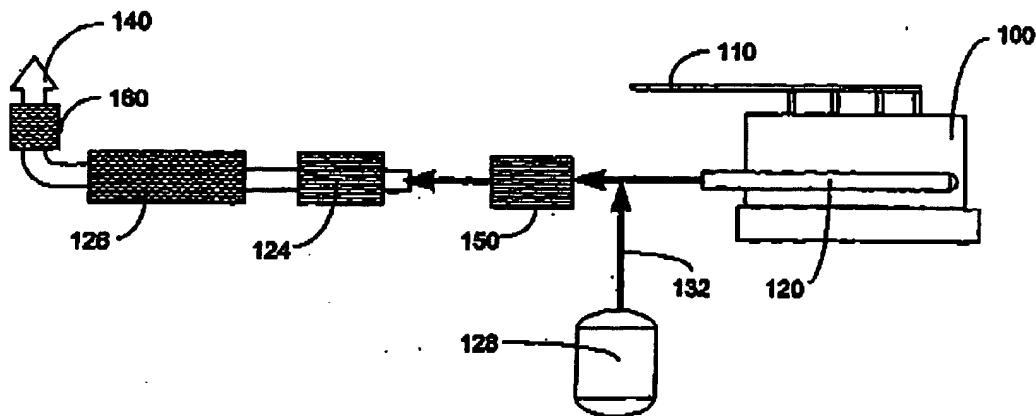


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: **SELECTIVE CATALYTIC NO<sub>x</sub> REDUCTION UTILIZING UREA WITHOUT CATALYST FOULING**

## (57) Abstract

Urea is used to reduce NO<sub>x</sub> in an SCR process with no risk of catalyst fouling. The urea is introduced from tank (128), through line (132) into the combustion gases as an aqueous urea solution at a location in the exhaust manifold/passage (120) where the combustion gases exhibit a temperature of from 250° to 1200 ° F. Following the introduction of the aqueous solution of urea, the combustion gases in the exhaust manifold/passage (120) are directed through a foraminous structure (124) that traps any water or urea that have not been gasified. Then, the combustion gases are directed through an NO<sub>x</sub>-reducing catalyst structure (126).

**DESCRIPTION****SELECTIVE CATALYTIC NO<sub>x</sub> REDUCTION  
UTILIZING UREA WITHOUT CATALYST FOULING****Related Applications**

5        This application is a continuation-in-part of copending and commonly-assigned U.S. Patent Application No. 08/518,251 entitled Method for Reducing Emissions of NO<sub>x</sub> and Particulates from a Diesel Engine, filed August 23, 1995, by J. D. Peter-Hoblyn, which in turn is a continuation of copending and commonly-assigned U.S. Patent Application No. 08/089,838  
10      filed July 12, 1993, filed internationally (PCT) and published as WO 95/02655 on January 26, 1995.

**Technical Field**

15      The invention provides a process for the safe, economical utilization of selective catalytic reduction (SCR) technology for nitrogen oxides (NO<sub>x</sub>) emissions. In particular, SCR technology is improved by eliminating the need for ammonia, which is dangerous, or other costly alternatives to it. The invention permits the use of urea in SCR systems by eliminating the possibility of catalyst fouling and/or deactivation.

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Combustion of carbonaceous materials for power generation, heat and/or waste disposal in boilers, incinerators, diesel engines, and turbines is typically conducted at such high temperatures that free radicals of nitrogen are combined with free oxygen to form NO and other nitrogen oxides species. 5 These nitrogen oxides are known generically as NO<sub>x</sub> and can also be formed by the oxidation of nitrogen present in the fuel. The art has made efforts to reduce all species.

It has long been known that ammonia can be used in catalytic and noncatalytic processes to reduce the concentration of NO<sub>x</sub> in combustion 10 gases. Unfortunately, ammonia is dangerous – it is both explosive and toxic. Replacements for ammonia have been suggested but, typically, they add costs and/or complexities in terms of additional processing or equipment requirements.

Urea can be a safe alternative to ammonia in some NO<sub>x</sub> reduction 15 processes. Under normal operating conditions and with proper control and safeguards, urea is hydrolyzed or otherwise broken down by hot combustion gases into gaseous compounds and free radicals, principally NH<sub>3</sub> and HNCO. However, a concern has been raised for SCR processes that a possibility exists that process anomalies could cause the urea or products of partial 20 decomposition, to reach and foul the catalyst. Because catalysts are expensive, employing precious metals and special support structures, and catalyst activity is required to complete the desired reactions, it is important to protect them against fouling and deactivation.

There is a present need for improvements that will permit the use of 25 urea in an SCR process with reduced risk of catalyst fouling and/or deactivation.

**Background Art**

In a 1977 Tennessee Valley Authority report for the Electric Power Research Institute, the state of the NO<sub>x</sub> reduction art for utilities is reviewed, comparing forty-two wet and dry methods. The authors pointed out that SCR systems which employ ammonia have some advantages over wet systems, in that they don't create nitrate solutions, but are sensitive to particulates. These systems typically employ electrostatic precipitators, but particulates can still pass through and foul the catalyst. Faucett, Maxwell and Burnett; *Technical Assessment of NO<sub>x</sub> Removal Processes for Utility Application*, November 1977.

In U. S. Patent No. 3,900,554, Lyon reported that ammonia could be used to reduce NO<sub>x</sub> in a noncatalytic system, now termed selective noncatalytic reduction (SNCR). This process cannot achieve the 90% and above reductions that are possible with catalysts, but has been considered an improvement over SCR in situations where high reductions are not critical. The danger of dealing with ammonia is, however, a problem. Ammonia is the NO<sub>x</sub>-reducing agent of choice for turbines as in the system described in U. S. Patent No. 4,682,468 which calls for introduction of ammonia into the hot gases of a gas turbine and replacement of part of the secondary air by an inert gas.

In U. S. Patent No. 4,208,386, Arand, et al., disclose that urea, like ammonia, can be employed for SNCR systems. It is infrequently suggested for SCR systems because process anomalies can and have caused problems including the formation of deposits on the catalyst. The resulting damage would lessen system reliability, and regulatory approval could be more difficult to obtain. The application of urea-SNCR to turbines has not been successful due to fear of liquid impingement on blades.

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In U. S. Patent Nos. 4,978,514 and 5,139,754, Hofmann, Sun and Luftglass disclose that if urea is introduced into a combustion effluent under conditions effective for SNCR and for generating ammonia, a small-scale SCR can be operated for an overall effective process. This process enables NO<sub>x</sub> reduction rates which are close to those achieved with SCR, but with a small fraction of the catalyst cost. A drawback in some situations, though, is an inability to reach regions with the high temperatures necessary for the SNCR, a problem which can be complicated in combustors involving wide load fluctuations. If the temperature is not hot enough and if there is not a sufficient time for complete gasification, the urea could carry over to the catalyst. In a related process, Sun, Hofmann and Lin disclose the addition of an ammonia source after the SNCR section in U. S. Patent No. 5,286,467.

Diesels are relatively efficient internal combustion engines and, in many cases, would be ideal for electric power generation. Unfortunately, diesels are plagued by the problem of high NO<sub>x</sub> generation, and the various pollutants seem to be interrelated when confronted with primary measures like exhaust gas recirculation. In other words, reduction of one pollutant, such as NO<sub>x</sub>, will tend to increase others, such as carbon monoxide, particulates or unburned hydrocarbons. This is, of course, unsatisfactory. Where the combustion is controlled to minimize particulates – a result compatible with the use of SCR catalysts – NO<sub>x</sub> is increased and makes the high NO<sub>x</sub> reduction obtainable by SCR necessary.

The art has long sought a safe and effective secondary measure, such as SNCR or SCR, to control diesel engine NO<sub>x</sub> in a manner that would permit diesels to gain more extensive use, justified by efficiency. Unfortunately, the temperature of combustion gases exiting the engine are not high enough for SNCR, and application of urea SCR technology would risk fouling the

catalysts. Until now, the application of urea SCR to diesel engines has required the use of large pyrolyzation chambers or other devices, as disclosed in European patent specification 558,452 A1. In WO 95/02655, I proposed the placement of a diesel particulate trap between the point of urea injection and an SCR catalyst. That solution is viewed as more practical than supplementary equipment of the type described in the above-noted European specification. However, particulate traps may not be required where combustion modifications adequately control particulates, but something other than devices of the noted European specification would be necessary to permit the use of urea in an SCR system. Despite the potential advantages of urea as a feed for SCR systems, it is not yet considered practical.

The art as it now stands continues to look at ammonia as the most suitable chemical for SCR processes – just as it has for the past several decades – whether in gaseous form as traditionally employed or as an aqueous solution prepared by the complete hydrolysis of urea. Unfortunately, the requirement that catalytic reactions be conducted in the presence of ammonia, means that a system for supplying ammonia gas safely to the effluent in the area of the catalyst must be developed and installed.

The use of ammonia in the manner of the prior art – whether as a gas or aqueous solution – carries with it the possibility of leakage and associated health and safety problems. The development of a process which would permit the use of urea in an SCR process simply, reliably, economically, and safely for both man and catalyst, is an advance the art is awaiting.

#### Disclosure of Invention

It is an object of the invention to provide a safe, reliable SCR system.

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It is another object of the invention to eliminate the safety problems associated with the storage and handling of ammonia.

5 It is another object of the invention to permit the introduction of urea into a combustion effluent at temperatures suitable for SCR, without fear of catalyst fouling.

It is another object of the invention to enable the protection of SCR equipment so effectively that urea can be employed over a wide temperature window without damaging the catalyst.

10 It is yet another and more specific object of the invention to eliminate the dangers associated with the use of ammonia for reducing NO<sub>x</sub> from the effluents of boilers, incinerators, turbines, diesel engines, and other stationary sources, by the use of urea and an SCR system.

15 These and other objects are achieved by the present invention which provides an improved process and apparatus for reducing the concentration of NO<sub>x</sub> contained in the combustion gases resulting from the combustion of a carbonaceous fuel. The process, in one of its aspects comprises: (a) introducing an aqueous solution containing urea into the combustion gases at a location where the combustion gases exhibit a temperature of from 250° to 1200°F to cause gasification of at least a portion of the urea; (b) following the introduction of the aqueous solution of urea therein, directing the combustion gases through a foraminous structure configured to capture water, urea or nongaseous byproducts of urea; and (c) then, directing the combustion gases through a NO<sub>x</sub>-reducing catalyst structure.

20

It is preferred that the urea solution be of a concentration and droplet

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size which permits convenient handling and disposal of the

PAGE 8/24 \* RCVD AT 3/29/2005 10:05:19 AM [Eastern Standard Time] \* SVR:USPTO-EFXRF-1/1 \* DNIS:8729306 \* CSID:7037377813 \* DURATION (mm:ss):06:08

distribution and rapid gasification in the combustion gasses. Preferably, the aqueous solution of urea is introduced as droplets having a number average diameter of less than 500  $\mu$ , preferably of from 5 to 100  $\mu$ , Sauter mean diameter. It is also preferred that the concentration of the solution be greater  
5 than about 10%, e.g., from about 15 to about 35%, urea. These parameters are critical where the introduction is made at a location where the combustion gases have a temperature of under 1000°F. To achieve the best balance of NO<sub>x</sub> reduction and low ammonia breakthrough, the aqueous urea solution is preferably introduced to give an NSR of from 0.5 to 1.5. The term "NSR"  
10 refers to the normalized stoichiometric ratio of the equivalents of nitrogen in the NO<sub>x</sub>-reducing agent to the equivalents of nitrogen in the NO<sub>x</sub> in the effluent being treated.

The apparatus of the invention will comprise: injector means for introducing an aqueous urea solution into combustion gases at an  
15 introduction location where the effluent is at a temperature of from 250° to 1200°F; a foraminous structure capable of capturing any water or urea which are not gasified by the combustion gases by the time it reaches said structure, the foraminous structure positioned downstream of the introduction location; and a NO<sub>x</sub>-reducing catalyst structure positioned downstream of the  
20 foraminous structure, said catalyst comprising a support and a catalyst carried thereon, the catalyst being characterized by its ability to catalyze a selective reaction between NH<sub>3</sub> and NO<sub>x</sub> to yield N<sub>2</sub> and H<sub>2</sub>O.

According to the preferred aspects of the process and apparatus, the  
25 space velocity of combustion gases through the NO<sub>x</sub>-reducing catalyst is greater than 5,000 hr<sup>-1</sup>, and preferably greater than 10,000 hr<sup>-1</sup>. It is also preferred to maintain the pressure drop across the foraminous structure to

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less than 0.5 psi. The space velocity through the foraminous structure is preferably greater than 10,000 hr<sup>-1</sup>.

It is an advantage of the invention that it is now possible to use urea, without the fear of catalyst fouling, to reduce nitrogen oxides by at least 80%, 5 preferably at least 90%, while controlling escape of ammonia with the effluent at a concentration of less than 10 ppm. It is an advantage of a preferred aspect of the invention to do this while also providing a catalyst effective to oxidize carbon monoxide to carbon dioxide.

**Brief Description of The Drawings**

10 The invention will be better understood and its advantages will be better appreciated from the following detailed description, especially when read in light of the accompanying drawings, wherein:

Figure 1 is a schematic view of one embodiment of the invention; and

15 Figure 2 is a schematic view of an alternative embodiment of the invention employing an SCR on a diesel engine.

**Detailed Description of The Invention**

By the term "urea solution" is meant a solution comprising urea in significant concentration as compared to the total solution solids. For example, the aqueous urea solution will preferably include urea in an amount 20 of at least 20% of the dissolved solids, which can also include ammonium salts such as carbonate, bicarbonate, and carbamate.

5       The invention has its greatest utility where the solution contains urea in such relatively large amounts that not all of it can be hydrolyzed or otherwise broken down by the hot combustion gases. The solution will contain water and a practical level of urea, e.g., from about 5 to about 60%, more typically from 10% to 50%, and preferably from about 15 to about 35%, urea by weight. Solutions which are fully saturated, or nearly so, can be used with greater practically by the invention because any urea that is not converted to gas-phase compounds or free radicals, will be effectively screened from the catalyst.

10      Figure 1 is a schematic view of one embodiment of the invention and shows a large combustor 10 of the type used for producing steam for electrical power generation. Fuel is burned with air in a combustion zone 20 and hot combustion gases rise and flow past heat exchangers 22, which transfer heat from the combustion gases to water for the generation of steam. 15      The combustion gases will contain NO<sub>x</sub> which is generated by the heat of combustion alone or due to the presence of nitrogen-containing compounds in the fuel.

20      Following passage from the heat exchangers 22, the combustion gases are often cooled to an extent that SNCR procedures cannot be effectively employed. The invention makes it possible to reduce the NO<sub>x</sub> concentration in the combustion gases by the use of urea SCR without concern for catalyst fouling. This is made possible by placing a foraminous structure 24 just upstream of the catalyst 26, 26' and 26". The foraminous structure 24 has the capability of capturing any urea or byproducts of it that have not been fully gasified. The foraminous structure collects these non-gaseous components and holds them until they become gasified. If not fully gasified, they will simply reside in their final form on the foraminous structure 24 and not on the NO<sub>x</sub>-reducing catalyst 26, 26' and 26" where they would

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cause fouling. While the drawing shows three catalyst sections, this is for purposes of illustration only and is not meant to be limiting of the invention.

The foraminous structure 24 can be any suitable material such as ceramic or metal, e.g., gauze, or the like, but is preferably an uncatalyzed foraminous material of the type used as an SCR catalyst support or, desirably, such a support with spent catalyst. It can include a catalytic material effective to hydrolyze the urea and/or remove soot by oxidation. It is an advantage of the invention that a spent catalyst can be installed at a position just upstream of the SCR catalyst. This advantage has significant practical value because, the SCR catalyst units can be installed to place the freshest ones nearest the outlet, successively moving them upstream as they age until the support which is in the position of foraminous structure 24 is essentially spent catalyst.

The catalyst 26, 26' and 26" downstream of the structure 24 will be the active catalyst for the particular design configuration and the structure 24, can be essentially inert. It will be recognized that while spent catalysts do have some activity, that does not disqualify them from use as the foraminous structure 24 of the invention. Desirably, a catalyst will not be considered spent and used for the foraminous structure unless it has suffered at least a 25%, typically 50%, loss in activity. The catalyst 26, 26' and 26" has 100% of the predetermined activity necessary to achieve a predetermined degree of NO<sub>x</sub>. The uncatalyzed support material 24 will typically have a volume of from 5 to 50% of that of the SCR catalyst.

In a typical operation, urea is stored for use as an aqueous solution, such as in tank 28. The urea solution can be at the concentration desired for use or it can be concentrated for dilution at the time of use. It can also be stored dry and hydrated to the desired degree on an as-needed basis. The

solution can be fed to one or more injectors, such as nozzles 30, 30' by lines 32, 32'. The nozzles can be of conventional design for spraying solutions and can be of the liquid-only or liquid and gas design. Where nozzles of the liquid and gas type are employed, internal mix nozzles are preferred to assure  
5 consistency of droplet size.

Flow to the nozzles 30, 30' is controlled such as by a controller unit 34. Sensors 36 and 36' are typically employed to sense a condition, such as temperature or gaseous component concentration, and generate a signal responsive to it. That signal is then compared to a reference value by the  
10 controller, and a control signal is generated based on the comparison. The control signal can adjust flow, pressure, concentration and/or other characteristic of the urea solution by operating appropriate control devices such as valves 38 and 38'.

The NO<sub>x</sub> levels can be preprogrammed into the controller 34 based on  
15 tested NO<sub>x</sub> values for given fuel flows and related parameters, or a sensor and related controls can be provided to provide real-time readouts.  
Preferably, a sensor means is provided to correct preprogrammed values.

The SCR catalyst used is one capable of reducing the effluent nitrogen oxides concentration in the presence of the breakdown products of urea,  
20 principally ammonia and HNCO. These include, for instance, activated carbon, charcoal or coke, zeolites, vanadium oxide, tungsten oxide, titanium oxide, iron oxide, copper oxide, manganese oxide, chromium oxide, noble metals such as platinum group metals like platinum, palladium, rhodium, and iridium, or mixtures of these, e.g., V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>. Other SCR catalyst materials conventional in the art and familiar to the skilled artisan can also be utilized.  
25 These SCR catalyst materials are typically mounted on a support such as a ceramic substance, a zeolite, or a homogeneous monolith, although other art

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known supports can also be used and the catalytic material can be present as a monolith.

Among the useful SCR catalysts are those described in the representative prior art processes below. Selective catalytic reduction processes for reducing NO<sub>x</sub> are well known and utilize a variety of catalytic agents. For instance, in European Patent Application EP 210,392, Eichholtz and Weiler discuss the catalytic removal of nitrogen oxides using activated charcoal or activated coke, with the addition of ammonia, as a catalyst. Kato et al. in U.S. Patent No. 4,138,469 and Henke in U.S. Patent No. 4,393,031 disclose the catalytic reduction of NO<sub>x</sub> using platinum group metals and/or other metals such as titanium, copper, molybdenum, vanadium, tungsten, or oxides thereof with the addition of ammonia to achieve the desired catalytic reduction.

Another catalytic reduction process is disclosed by Canadian Patent No. 1,100,292 to Knight which relates to the use of a platinum group metal, gold, and/or silver catalyst deposited on a refractory oxide. Mori et al. in U.S. Patent No. 4,107,272 discuss the catalytic reduction of NO<sub>x</sub> using oxysulfur, sulfate, or sulfite compounds of vanadium, chromium, manganese, iron, copper, and nickel with the addition of ammonia gas.

In a multi-phased catalytic system, Ginger, in U.S. Patent No. 4,268,488, discloses exposing a nitrogen oxides containing effluent to a first catalyst comprising a copper compound such as copper sulfate and a second catalyst comprising metal combinations such as sulfates of vanadium and iron or tungsten and iron on a carrier in the presence of ammonia.

The ammonia-containing effluent is most preferably passed over the

about 950°F, preferably at least 550°F. In this manner, the ammonia and other active gaseous species present in the combustion gases due to the introduction of the urea solution most effectively facilitates the catalytic reduction of nitrogen oxides. The effluent will preferably contain an excess of oxygen, e.g., from about 1 to about 10%.

5 Use of the present invention with any of the above SCR catalysts (the disclosures of which are specifically incorporated by reference) reduces or eliminates the requirement for the transport, storage and handling of large amounts of ammonia or ammonium water.

10 An oxidation catalyst (not shown) can be positioned downstream of the SCR catalyst 20 for the purpose of eliminating ammonia which might otherwise pass through the system and provide an objectionable odor. Among the catalysts suitable for this purpose are oxidation catalysts.

15 It is another advantage of the invention that when the principles are applied to combustion gases emanating from a diesel engine, the need for a diesel particulate trap may be eliminated by operation of the engine under conditions which reduce the particulates to acceptably low levels, preferably less than 0.05 grams per horsepower-hour, and then reducing the NO<sub>x</sub> by the use of a safe SCR system utilizing urea.

20 Figure 2 shows a diesel engine 100 having a fuel supply line 110 and an exhaust manifold/passage 120 directing combustion gases as exhaust from the engine to an exhaust system including a foraminous structure 124 directly upstream of a NO<sub>x</sub>-reducing SCR catalyst 126, which in turn is ahead of a tall pipe 140 through which the combustion gases are exhausted to the atmosphere. The diesel fuel is injected into the cylinders where it ignites in the presence of the air which has been heated due to compression within the

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cylinders. A catalyst 160 is shown provided downstream of the SCR catalyst to oxidize any ammonia that would otherwise pass through the SCR catalyst.

The arrangement of Figure 2 enables reducing the emissions of NO<sub>x</sub> from a diesel engine by assuring the hydrolyzation and/or pyrolyzation, or 5 otherwise gasification of urea in the exhaust system prior to entry into the SCR catalyst unit 126. An aqueous urea solution is introduced from tank 128, through line 132. Desirably, a static mixer 150 is positioned between the point of injection and the NO<sub>x</sub>-reduction catalyst. Once gasified, the gaseous components are introduced into foraminous structure 124 mounted directly in 10 the exhaust system, to capture any nongaseous urea or urea byproducts and utilize the heat of the exhaust gases to gasify them. The active gaseous components are introduced into the exhaust gases upstream of an SCR catalyst. Additional heat for gasification can be supplied by an electric heater (not shown).

15 The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the invention, and it is not intended to detail all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such obvious modifications and variations be included within 20 the scope of the invention which is defined by the following claims. The claims are meant to cover the claimed elements and steps in any arrangement or sequence which is effective to meet the objectives there intended, unless the context specifically indicates the contrary.

**CLAIMS**

- 1. A process for reducing the emissions of nitrogen oxides from a combustor wherein carbonaceous material is burned in the presence of oxygen to produce combustion gases including NO<sub>x</sub>, the process comprising:**
  - 5 (a) introducing an aqueous urea solution into the combustion gases at a location where the combustion gases exhibit a temperature of from 250° to 1200°F;**
  - (b) following the introduction of the aqueous solution of urea therein, directing the combustion gases through a foraminous structure configured to capture water, urea or nongaseous byproducts of urea; and**
  - (c) then, directing the combustion gases through a NO<sub>x</sub>-reducing catalyst structure.**
- 15 2. A process according to claim 1 wherein the aqueous solution of urea is introduced as droplets having a number average diameter of from 5 to 100 μ, sauter mean diameter.**
- 20 3. A process according to claim 1 wherein the combustion gases exhibit a temperature of from 500° to 1000°F at the location where the aqueous urea solution is introduced.**
- 4. A process according to claim 1 wherein the aqueous urea solution comprises water and from 5 to 60% urea.**
- 5. A process according to claim 1 wherein the aqueous urea solution is introduced to give an NSR of from 0.5 to 1.5.**

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6. A process according to claim 1 wherein the foraminous structure comprises a spent catalyst.
7. A process according to claim 1 wherein the catalyst further comprises a catalyst effective to oxidize carbon monoxide to carbon dioxide.
- 5 8. A process according to claim 1 wherein a catalyst effective to oxidize residual ammonia is positioned downstream of the NO<sub>x</sub>-reducing catalyst.
9. A process according to claim 1 wherein space velocity of combustion gases through the NO<sub>x</sub>-reducing catalyst is greater than 5,000 hr<sup>-1</sup>.
- 10 10. A process according to claim 1 wherein the space velocity through the foraminous structure is greater than 10,000 hr<sup>-1</sup>.
11. A process according to claim 1 wherein the pressure drop across the foraminous structure is less than 0.5 psi.
- 15 12. A process for reducing emissions of nitrogen oxides from the combustion gases resulting from burning carbonaceous matter in air under conditions which cause the production of thermal NO<sub>x</sub>, comprising:
  - (a) preparing an aqueous urea solution containing from 15 to 60% urea;
  - (b) introducing into the combustion gases at a temperature of from 500° to 1000°F, the urea solution as droplets having a number average diameter of from 5 to 100 μ, sauter mean diameter and an NSR of from 0.5 to 1.5 relative to the NO<sub>x</sub> present in the effluent;
  - 20 (c) following the introduction of the aqueous urea solution, directing the combustion gases at a space velocity of at least 10,000 hr<sup>-1</sup> through a

foraminous structure and through a catalyst for selective catalytic reduction at a space velocity of at least 10,000 hr<sup>-1</sup>.

13. A process according to claim 12 wherein the nitrogen oxides are reduced by at least 60% and the ammonia concentration of the combustion gases is  
5 less than 10 ppm.
14. A process according to claim 12 wherein the foraminous structure further comprises a catalyst effective to oxidize carbon monoxide to carbon dioxide.
- 10 15. A process according to claim 12 wherein the concentration of urea in the solution is less than about 25% by weight of the solution.
16. An apparatus for reducing emissions of nitrogen oxides from the combustion gases resulting from burning carbonaceous matter in air under conditions which cause the production of thermal NO<sub>x</sub>, comprising:
  - (a) means for introducing an aqueous urea solution into a combustion  
15 at an introduction location where the effluent at a temperature of from 400° to 1000°F;
  - (b) a foraminous structure capable of capturing any water or urea which are not gasified by the combustion gases by the time it reaches said structure, the foraminous structure positioned downstream of the introduction  
20 location and comprising a spent catalyst; and
  - (c) a NO<sub>x</sub>-reducing catalyst structure positioned downstream of the foraminous structure.
- 25 17. An apparatus according to claim 16, wherein: the foraminous structure further comprises a catalyst effective to oxidize carbon monoxide to carbon dioxide.

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18. Apparatus according to claim 16 wherein a catalyst effective to oxidize residual ammonia is positioned downstream of the NO<sub>x</sub>-reducing catalyst.
19. An apparatus according to claim 16, wherein the foraminous structure has catalytic activity to enhance the hydrolysis of urea.

## INTERNATIONAL SEARCH REPORT

International application No. PCT/US97/21107
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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E,Y	US 5,601,792 A (HUG et al.) 11 February 1997 (11.02.97), figures 1 and 6; column 2, lines 1 to end.	1-19
E,Y	US 5,489,419 A (DIEP et al.) 06 February 1996 (06.02.96), abstract, column 5, lines 36 to column 6, lines 1-64.	1-19
Y	US 4,138,469 A (KATO et al.) 06 February 1979 (06.02.79), abstract, column 2, line 62 to column 3, lines 1-11 and claim 1.	1-19
A	US 3,900,554 A (LYON) 19 August 1975 (19.08.75), abstract.	1-19
A	US 4,208,386 A (ARAND et al.) 17 June 1980 (17.06.80), column 3, lines 1-43.	1-19
A	US 4,393,031 A (HEINKE) 12 July 1983 (12.07.83), column 2, lines 35 - end.	1-19
A	US 4,997,631 A (HOFMANN et al.) 05 March 1991 (05.03.91), column 4, lines 29-62.	1-19
A	US 5,139,754 A (LUFTGLASS et al.) 18 August 1992 (18.08.92), column 2, line 63 to column 4, lines 1-25.	1-19
A	US 5,057,293 A (EPPERLY et al.) 15 October 1991 (15.10.91), column 5, lines 29-60.	1-19

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 8/00; C10B 21/00  
US CL :423/234.1, 244.09, 235; 60/280, 301, 295, 683, 317; 422/169

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/234.1, 244.09, 235; 60/280, 301, 295; 422/169  
60/317, 683

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

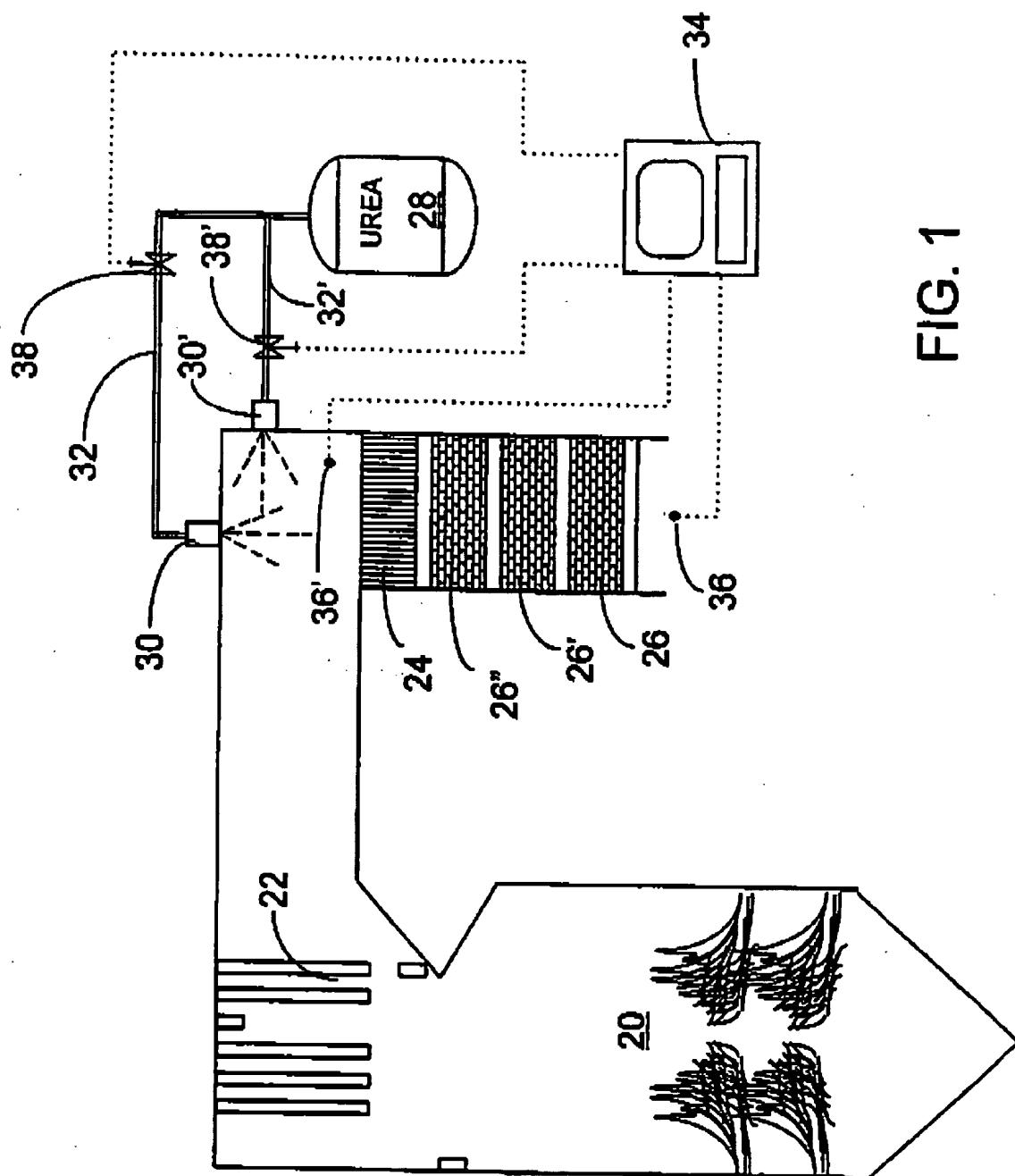
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,431,893 A (HUG et al.) 11 July 1995 (11.07.95), abstract, column 2, lines 62 - end and column 6, line 62 to column 7, lines 1-30.	1-19
Y	US 5,281,403 A (JONES) 25 JANUARY 1994 (25.01.94), abstract and column 4, line 30 to column 5, lines 1-40.	1-19
Y	US 5,266,083 A (PETER-HOBLYN et al.) 30 November 1993 (30.11.93), column 9, line 43 to column 10, lines 1-39.	1-19
Y	US 4,107,272 A (MORI et al.) 15 August 1978 (15.08.78), column 2, line 41 to column 2, lines 1-14 and claim 1.	1-19

<input checked="" type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input type="checkbox"/>	See patent family annex.
"T"	Special category of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"B"	earlier documents published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another claim(s) or other special reasons (as specified)	"A"	document member of the same patent family
"D"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
05 FEBRUARY 1998	13 MAR 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer <i>MARGARET S. MEDLEY</i>
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Form PCT/ISA/210 (second sheet)(July 1992)\*

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WO 98/22209

PCT/US97/21107

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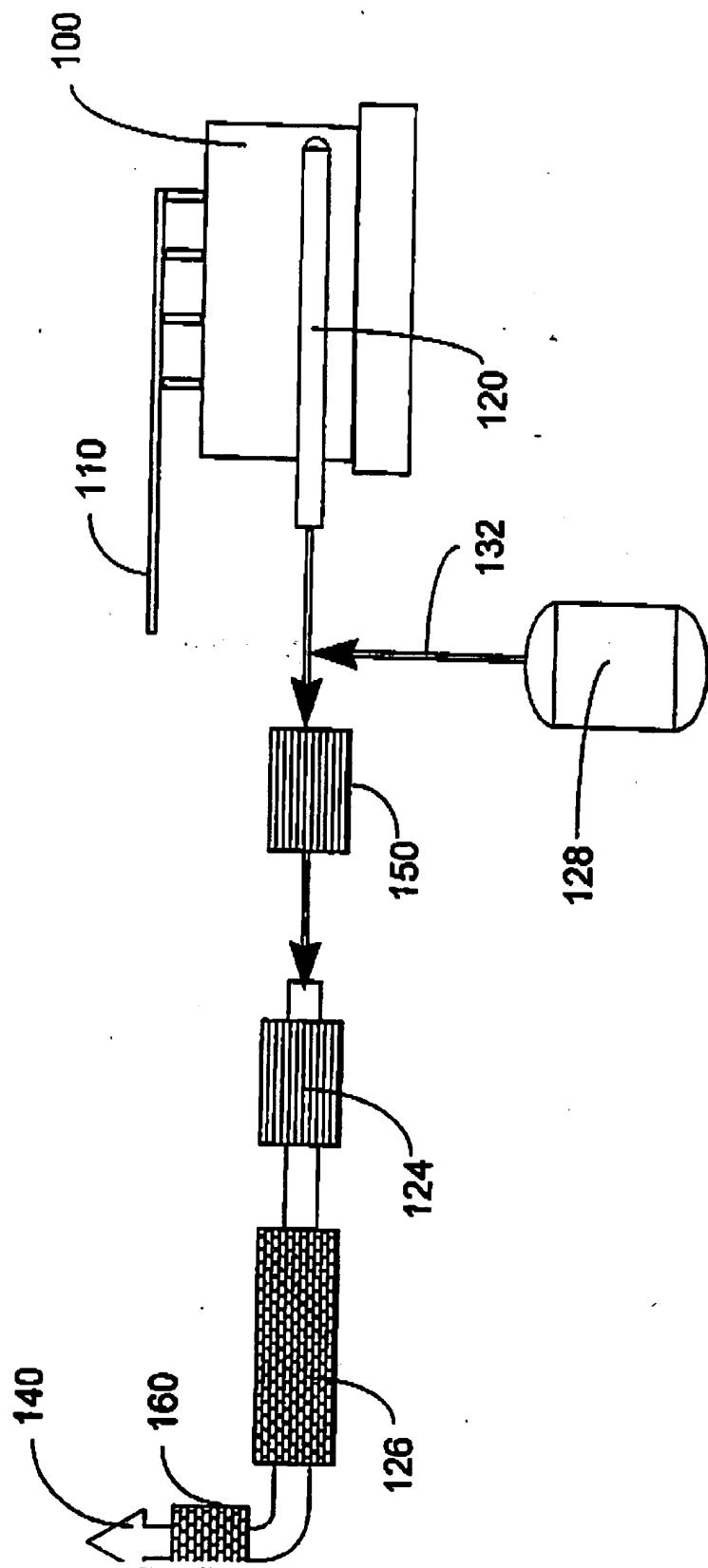


FIG. 2